APPLICATION OF PASSIVE SAMPLERS TO MONITOR REMEDIATION PROGRESS

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Passive samplers have been used as collection devices for measuring low concentrations of pollutants from air and water phases. Contaminant biouptake in benthic organisms and flux from contaminated sediments are controlled by the freely dissolved porewater chemical concentrations in sediment. The main challenges in measuring porewater concentrations of hydrophobic compounds such as PCBs and PAHs by direct extraction is the very low freely dissolved concentrations of these compounds and interference in the measurement from sorption to colloidal phases that are difficult to separate. Our recent work has explored the use of thin films of polyoxymethylene (POM) as equilibrium passive samplers to measure porewater concentrations of a range of toxic organic chemicals including PCBs, PAHs, dioxins, furans, and chlorinated pesticides in laboratory measurements and measurements conducted in the field. Using POM passive samplers we monitored changes in in-situ aqueous PCB concentrations over time at a pilot study site in a river where activated carbon was amended to sediment to reduce PCB bioavailability. Results of passive sampler monitoring in the field over four years indicated that amendment of activated carbon to sediments reduced porewater PCB concentration near the sediment surface to values lower than ambient concentrations in the overlying water. This finding reveals that amendment of strong sorbents may be effective in reversing the direction of chemical flux between contaminated sediment and overlying water locally during a pilot study. This talk will present an overview of the use of passive equilibrium samplers in laboratory assessment of aqueous equilibrium concentrations and use in the field to monitor changes in contaminant concentrations in the sediment porewater and overlying water.</td></tr>
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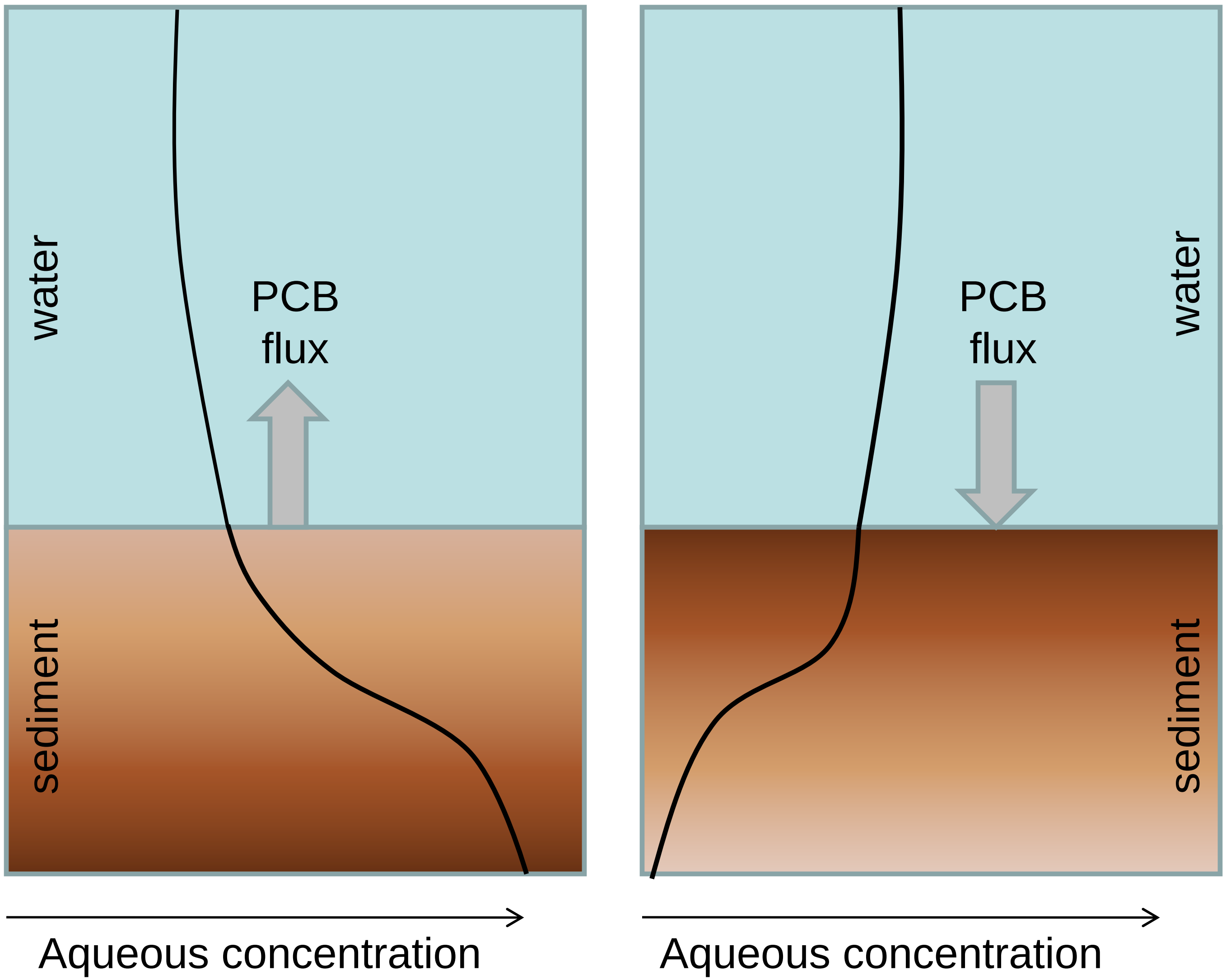
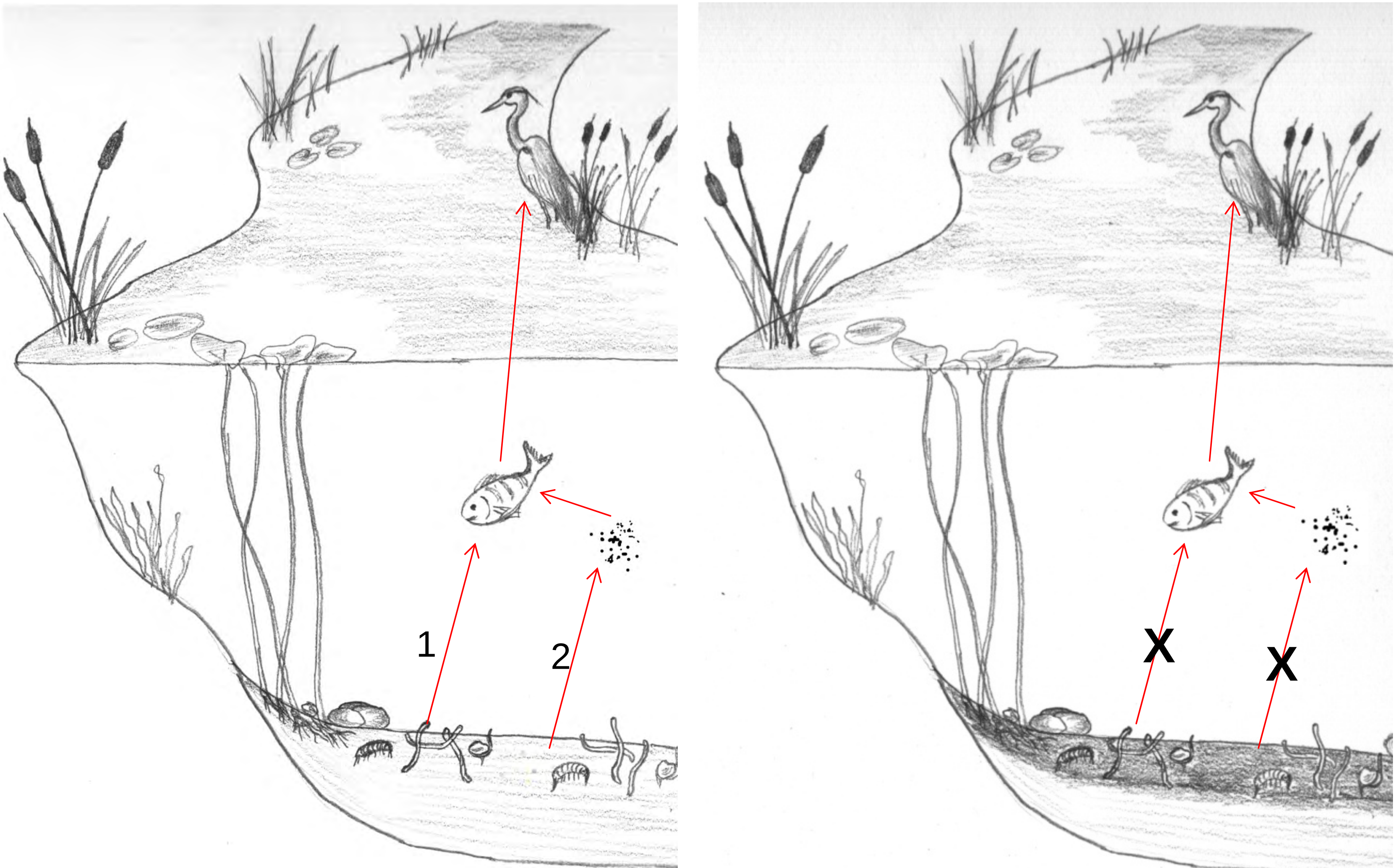
Conceptual model for PCB flux



Hunters Point example	Grasse River example
2 ng/L	10-30 ng/L

37 ng/L	100-1000 ng/L

PCB UPTAKE PATHWAYS TO FISH

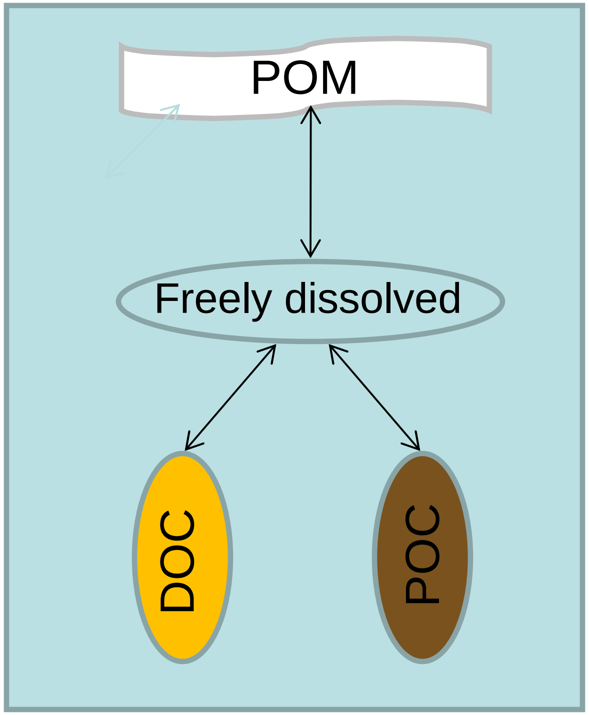


1: bioaccumulation in benthic organisms and ingestion by fish
2: flux into water column and uptake through the pelagic food chain

Partitioning of hydrophobic chemicals in sediment

1)Hydrophobic chemicals partition among the aqueous and different solid phases

2)Equilibrium distribution can be described by linear free energy relationships



$$C_{total} = C_{free} + C_{DOC} + C_{POC}$$

$$C_{total} = C_{free} + DOC{*}K_{DOC}{*}C_{free} + POC{*}K_{POC}{*}C_{free}$$

Two approaches to measure total and freely dissolved concentrations:

1)Remove POC by centrifugation/flocculation, measure total dissolved concentration and DOC, and estimate freely dissolved concentration.

2)Use calibrated passive sampler to estimate freely dissolved concentration, measure DOC, and estimate total dissolved concentration.

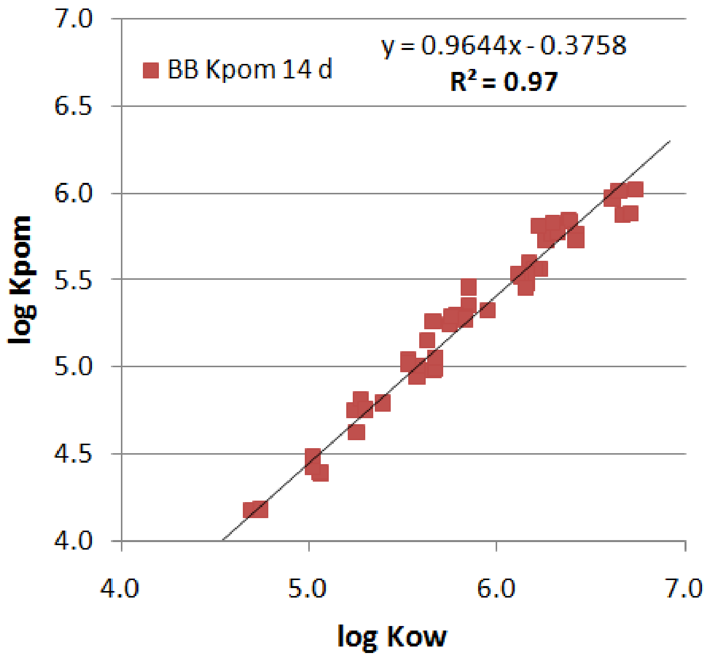
Passive sampler calibration

- Equilibrium passive samplers : measure freely dissolved aqueous concentration by partitioning

$$C_{aq} = K_{POM} * C_{POM}$$

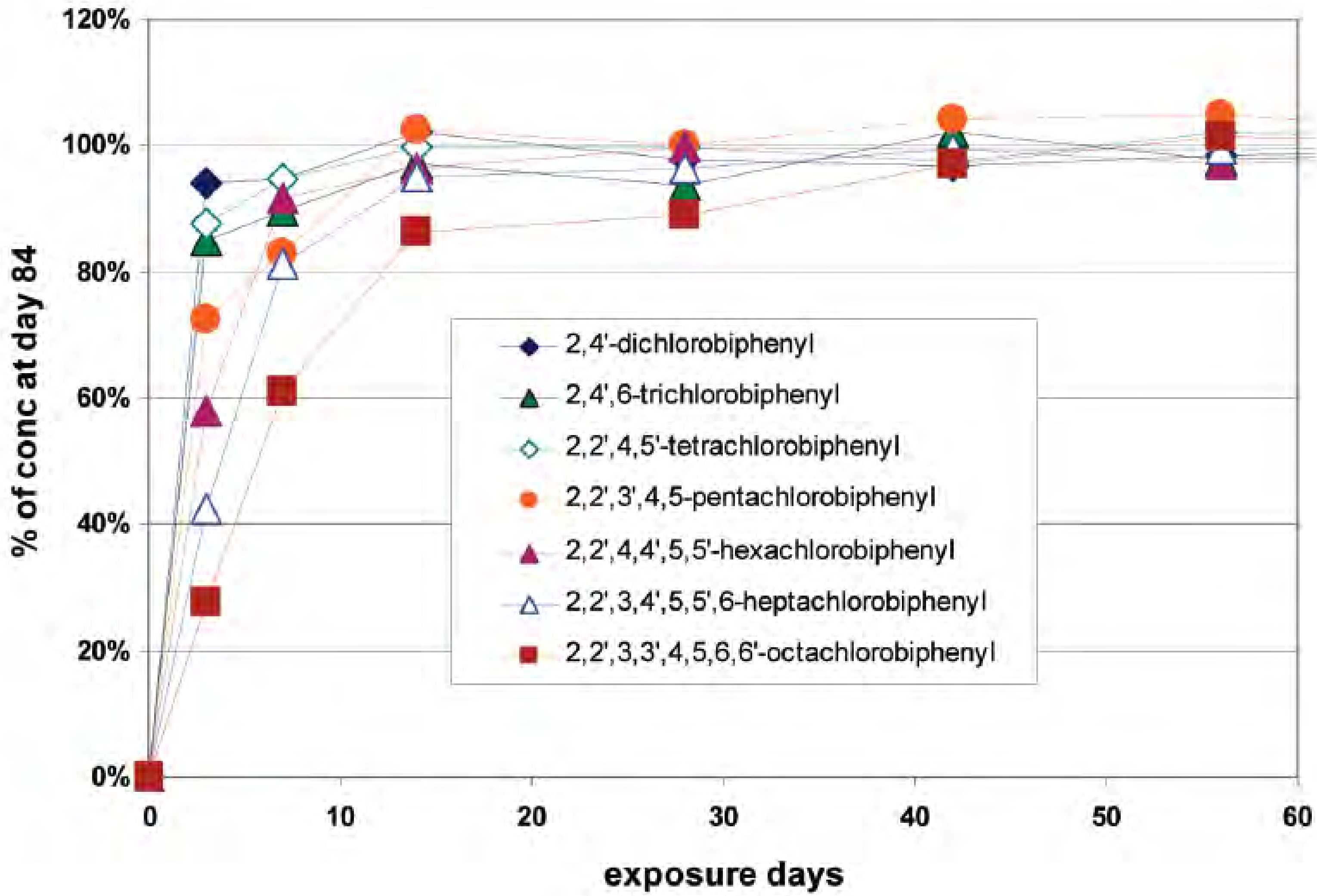
- Determine K_{POM} for suite of target analytes using equilibrium batch tests with POM in sediment-water slurry or in spiked water

- Performance reference compounds (PRCs) or other methods may be used to account for non-equilibrium conditions during field exposures



Example POM calibration for PCB congeners

PCB uptake kinetics in 76 mm POM sheets in sediment slurry



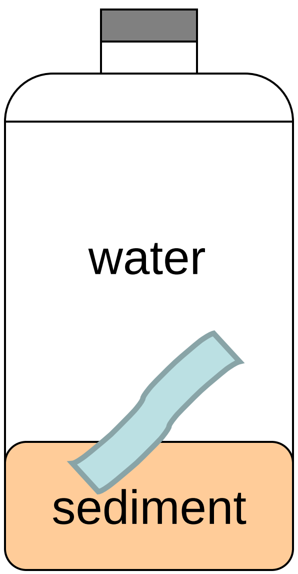
Hawthorne et al., Anal. Chem. 2009, 81, 9472–9480

Applications of passive sampling:

1) Batch equilibrium measurements for low aqueous concentrations (PCBs, PAHs, dioxins)

2) In-situ probing to assess ambient contaminant concentrations or to assess changes with time or with treatment

Pictures of typical applications:



Laboratory batch equilibrium

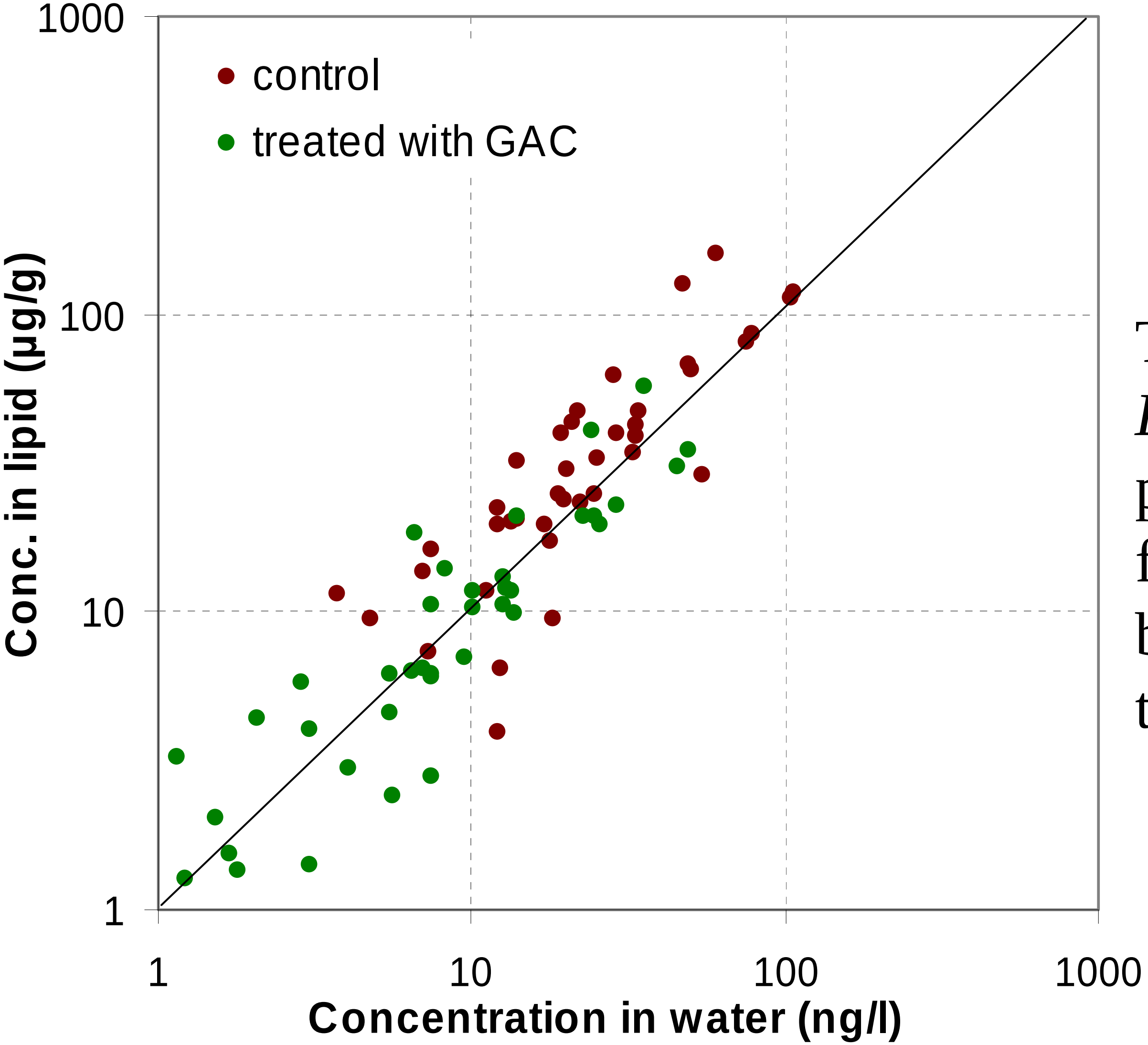
Stream water quality assessment

Field evaluation of treatment performance

Depth profiling of porewater conc. in sediment

Application 1: Batch equilibrium studies:

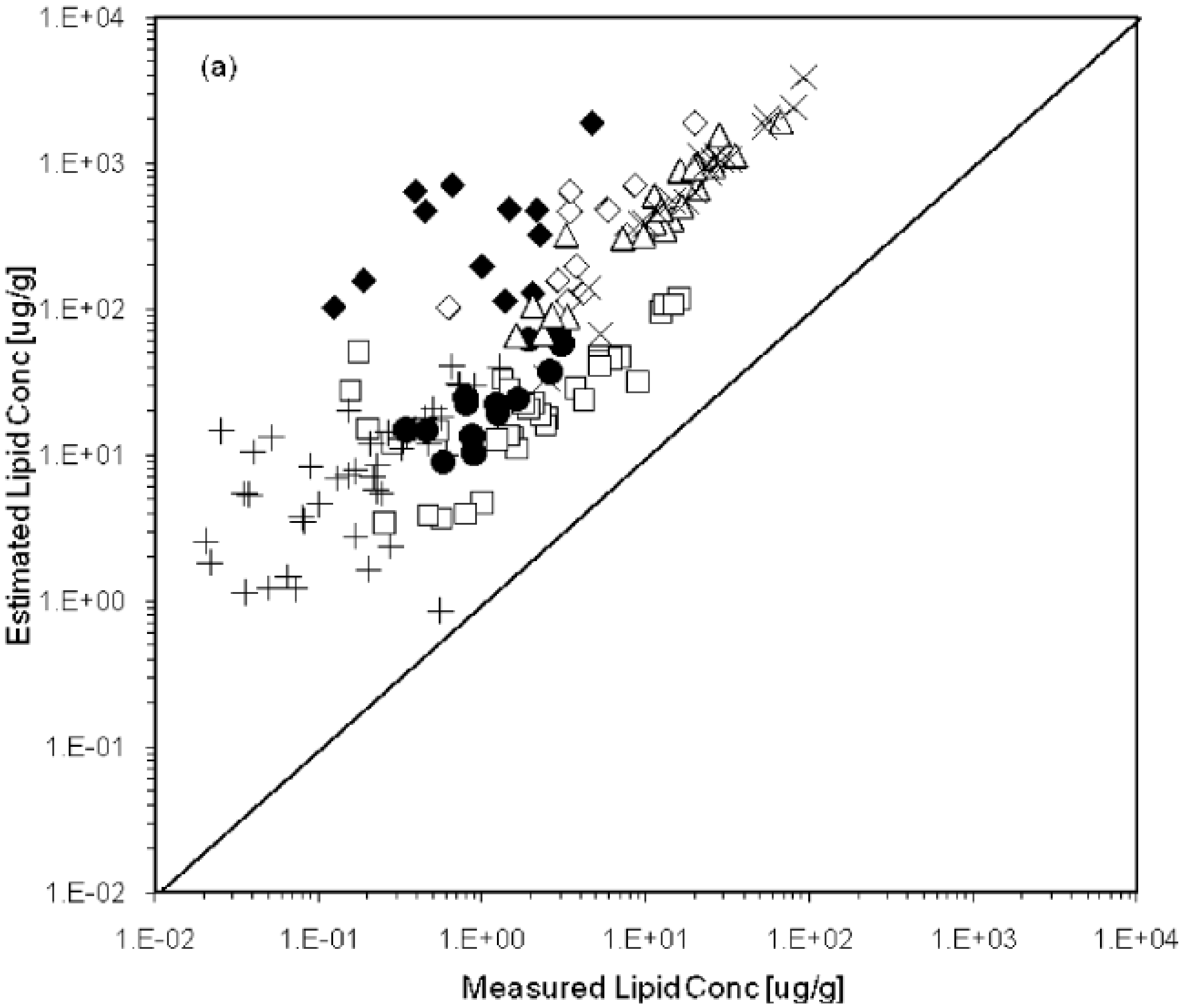
PCBs in sediment



Tetra PCB congeners in *L. variegatus* and porewater for three freshwater sediments before and after treatment with AC

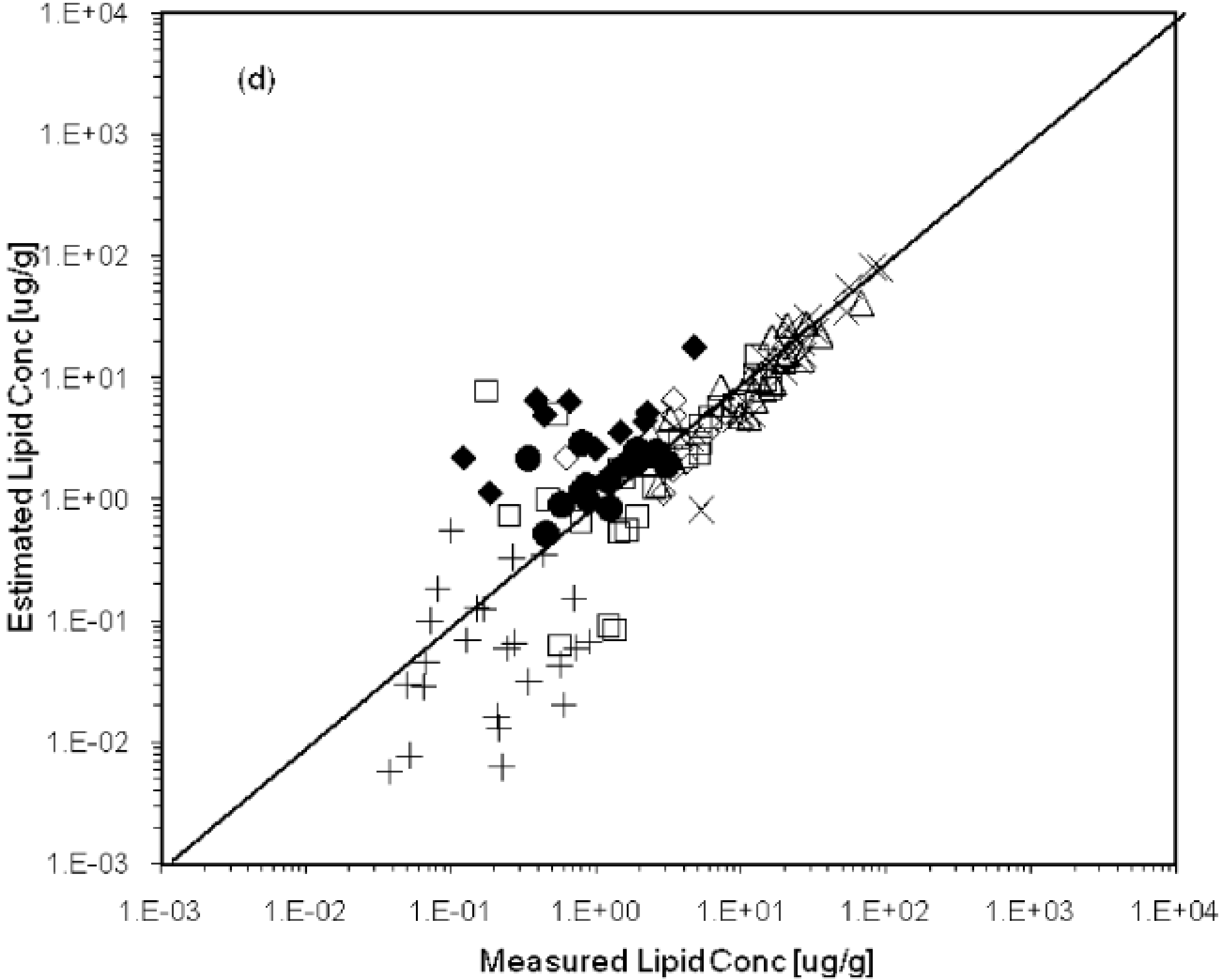
(Sun & Ghosh, ES&T 2008)

Estimating from sediment concentration



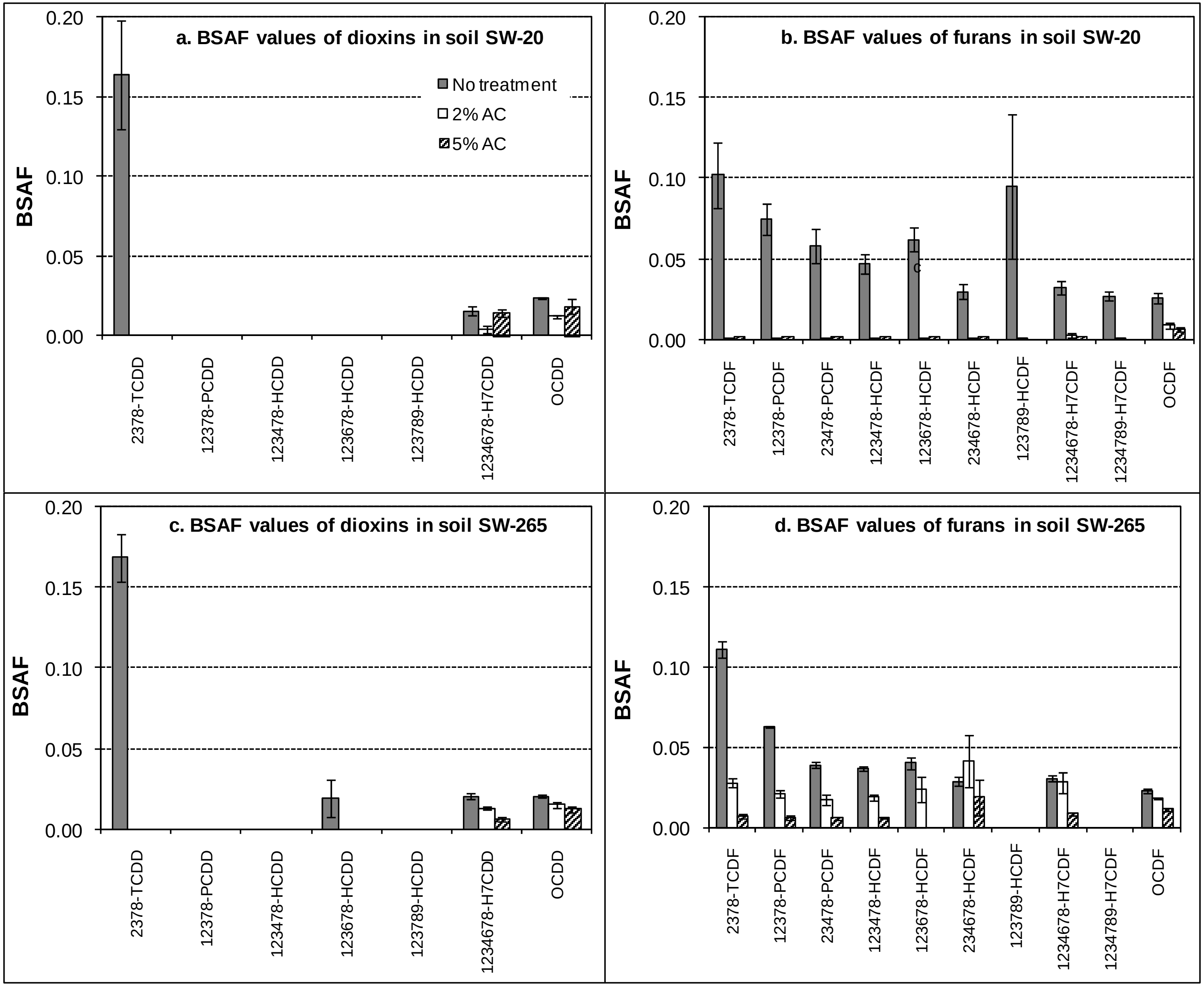
Werner et al. EST 2010

Estimating from equilibrium aqueous concentration



Werner et al. EST 2010

Application 1: Dioxins and furans bioaccumulation in earthworms from soil



(Fagervold et al., ES&T 2010)

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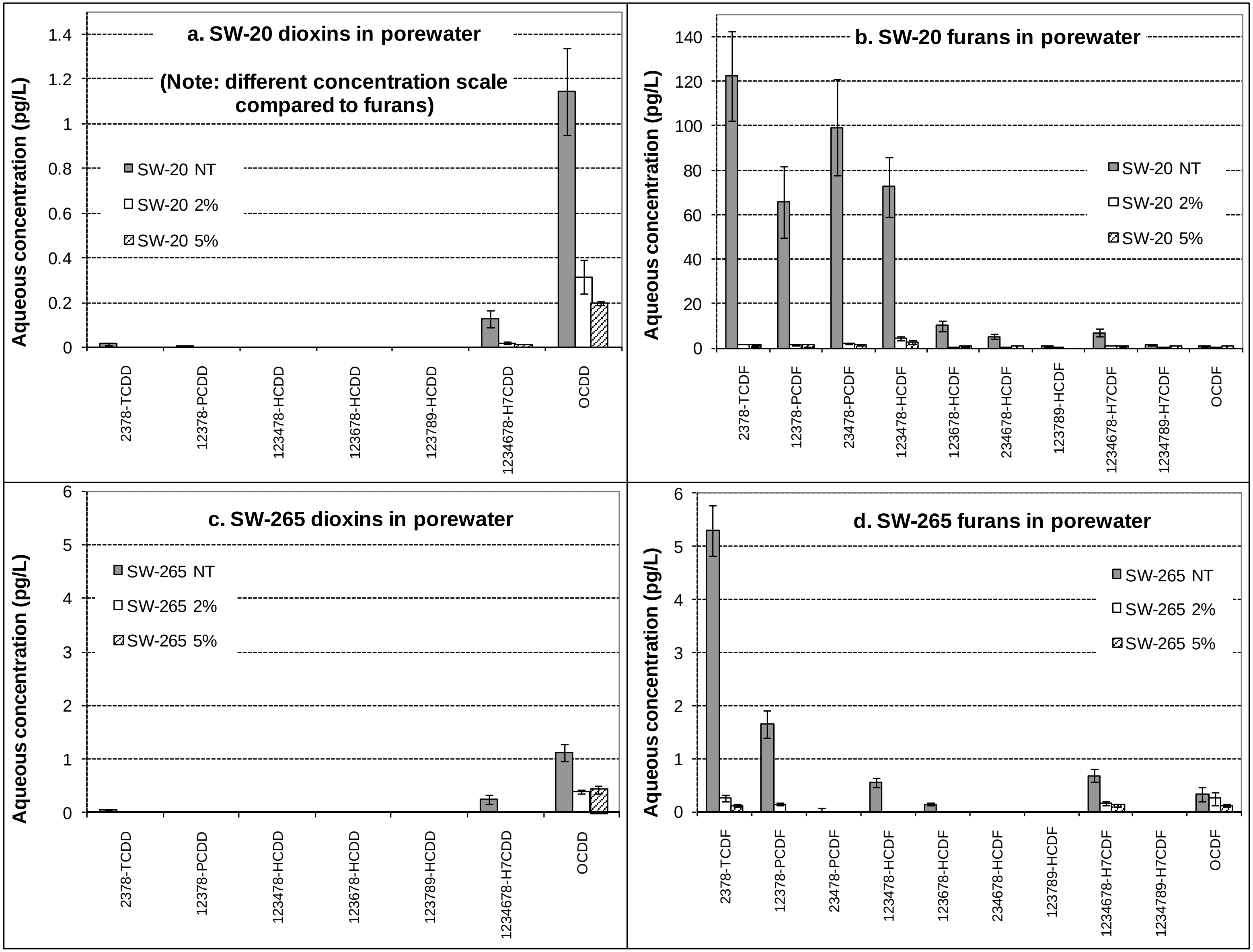
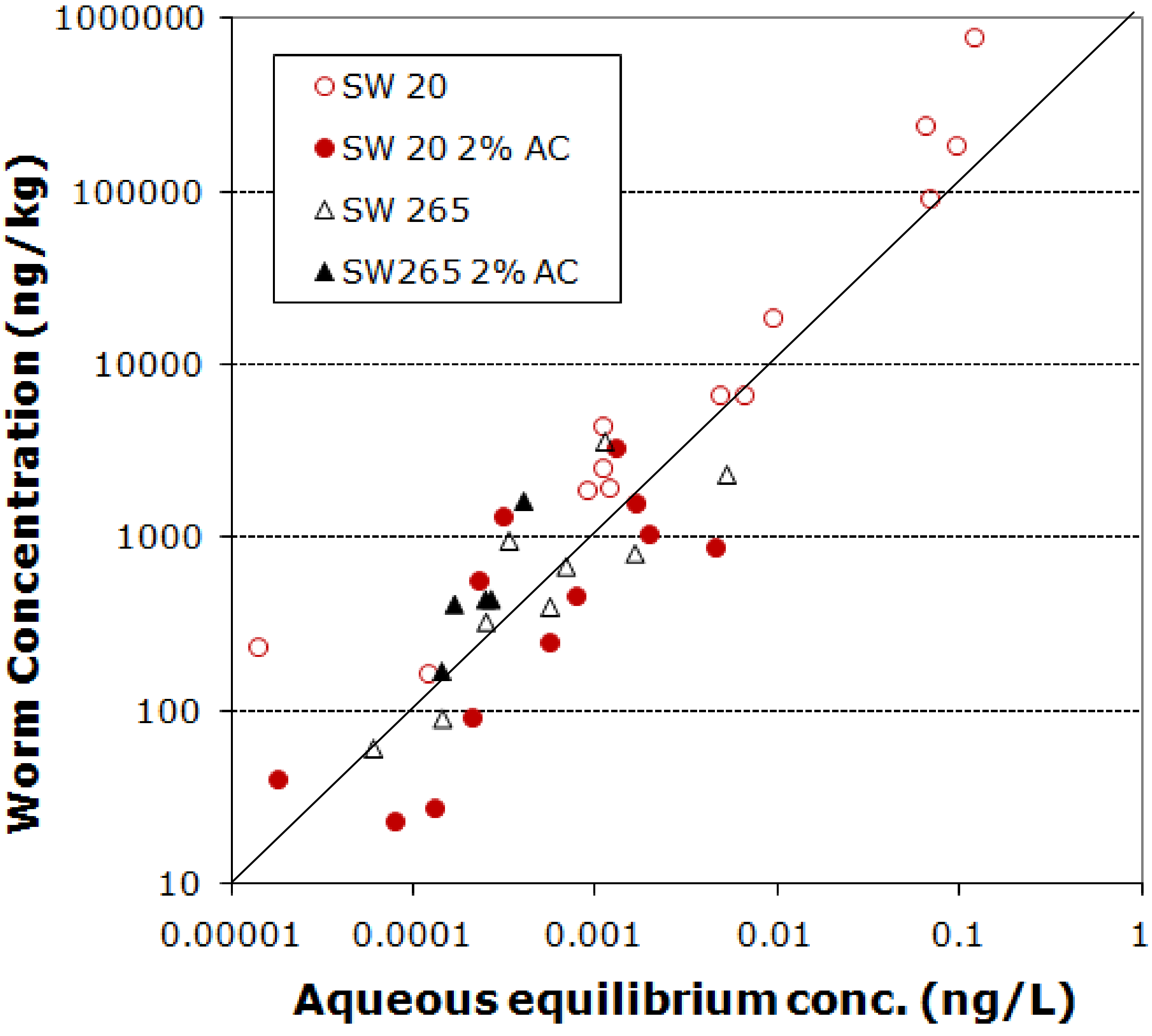


(Fagervold et al., ES&T 2010)

Application 1: Batch equilibrium studies with POM: Dioxins and furans in soil



Earthworm and equilibrium aqueous phase concentration in 2 soils before and after treatment with AC

(Fagervold et al., ES&T 2010)

Application 2: In-situ monitoring after sediment remediation

Pilot-scale field applications of activated carbon to reduce PCB bioavailability in contaminated sediments

- Grasse River, NY

- Hunters Point, CA

PILOT DEMONSTRATION IN GRASSE RIVER

(Participants: Alcoa, EPA, UMBC, Stanford University, Anchor Env., Brennan, Tetra Tech, Arcadis-BB&L, QEA)

Mixed Tiller (75’ x 100’)

Unmixed (50’ x 50’)

Tine Sled (50’ x 60’)

Initial testing area (50’ x 100’)

- L-shaped silt screen to minimize suspended particle transport
- Equipment mobilized on barges
- Target dose of activated carbon = 0.5x TOC in surficial sediments (+50% safety factor)
- No measurable change in water-column PCBs downstream
- Post-treatment monitoring for 3 years

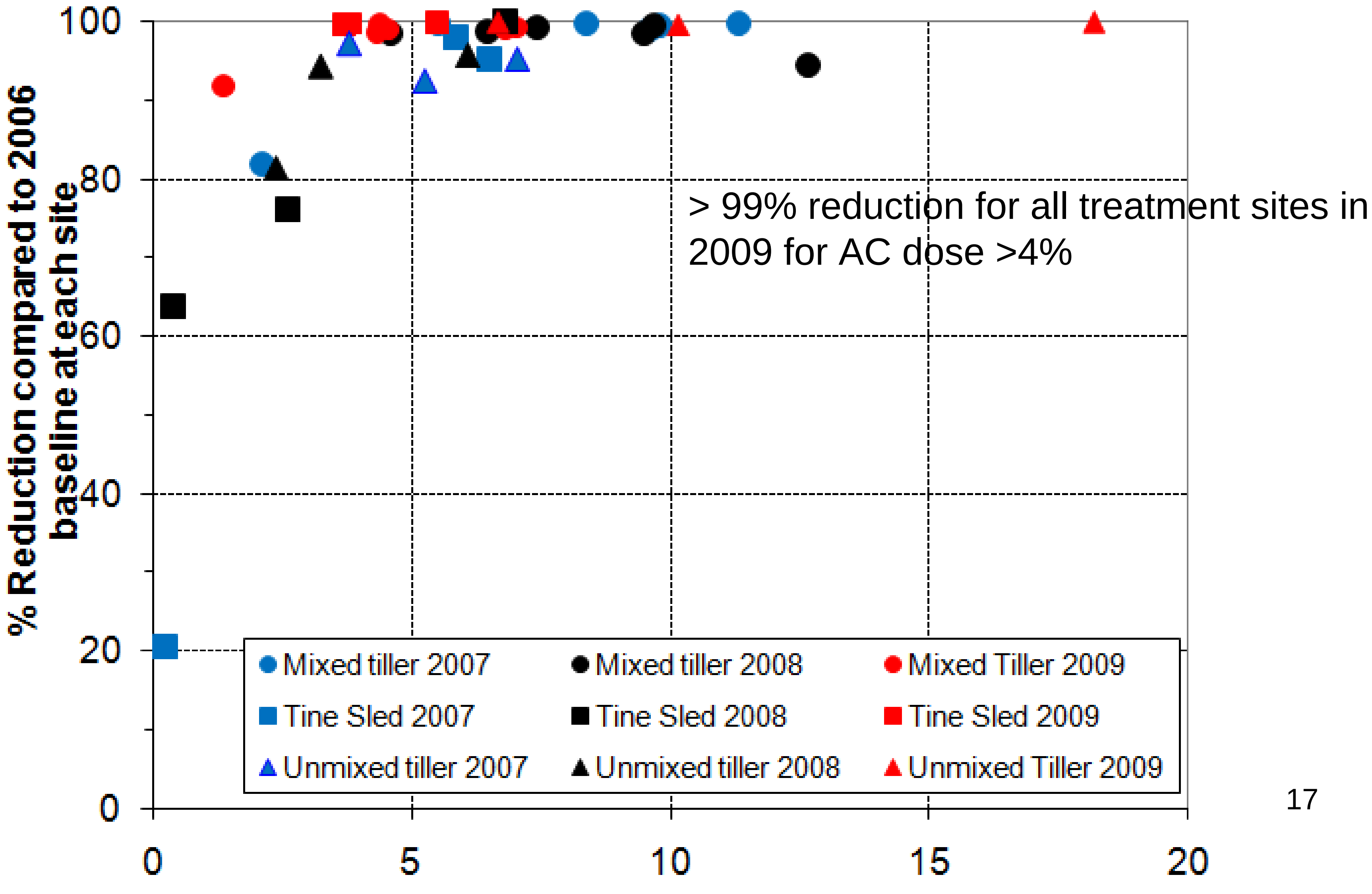
Grasse River: In-situ monitoring studies

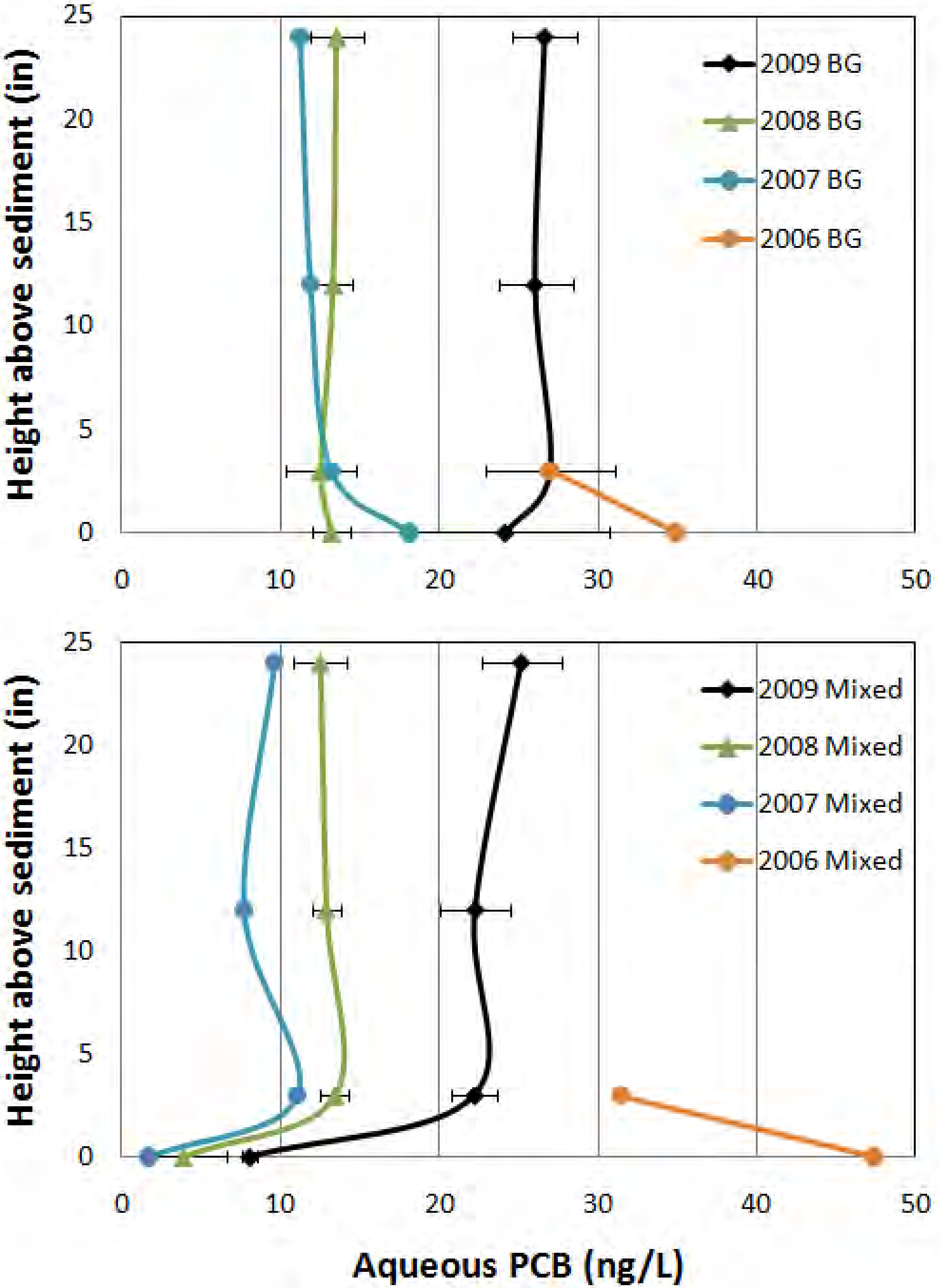
Grasse River, NY

- In-river baseline deployment of field exposure cages with *L. variegatus* using a method adapted from Burton et al. 2005
- Parallel deployment of POM passive samplers

L. variegatus

% REDUCTION IN WATER VS. AC DOSE





PCB IN WATER BASED ON IN-SITU PASSIVE SAMPLERS

Reduced aqueous PCB on sediment surface at AC treated sites compared to overlying water

Future research needs

- Better understanding of the diffusion process of PCBs, PAHs, dioxins through polymers
- Standardized (consensus) polymers that everyone can obtain and use easily
- Standardized calibration of polymers for a range of contaminants (PAHs, PCBs, dioxins, furans, pesticides)
- Better understanding of uptake kinetics in different exposure modes (water column vs in sediment)

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